

THE CLAIMS

What is claimed is:

1. A composition for cleaning semiconductor wafers, wherein the composition includes supercritical fluid and at least one additive selected from the group consisting of:

- (I) fluoro species; and
- (II) primary and/or secondary amine(s).

2. The composition of claim 1, comprising fluoro species.

3. The composition of claim 2, wherein the supercritical fluid comprises a supercritical fluid species selected from the group consisting of carbon dioxide, oxygen, argon, krypton, xenon, ammonia, methane, methanol, dimethyl ketone, hydrogen, forming gas, and sulfur hexafluoride.

4. The composition of claim 2, wherein the supercritical fluid comprises carbon dioxide.

5. The composition of claim 2, wherein the fluoro species comprises a fluorine-containing material selected from the group consisting of hydrogen fluoride (HF), ammonium fluoride (NH_4F), alkyl hydrogen fluoride (NRH_3F), dialkylammonium hydrogen fluoride ($\text{NR}_2\text{H}_2\text{F}$), trialkylammonium hydrogen fluoride (NR_3HF), trialkylammonium trihydrogen fluoride ($\text{NR}_3(3\text{HF})$), tetraalkylammonium fluoride (NR_4F), and xenon difluoride (XeF_2), wherein each R is independently selected from $\text{C}_1\text{-C}_8$ alkyl and $\text{C}_6\text{-C}_{10}$ aryl.

6. The composition of claim 2, wherein the fluoro species comprises triethylamine trihydrogen fluoride.

7. The composition of claim 2, wherein the fluoro species comprises ammonium fluoride.
8. The composition of claim 2, further comprising co-solvent.
9. The composition of claim 8, wherein the co-solvent comprises at least one solvent species selected from the group consisting of alcohols, amides, ketones, and esters.
10. The composition of claim 8, wherein the co-solvent comprises at least one solvent species selected from the group consisting of alcohols, N-alkylpyrrolidones, N-arylpyrrolidones, dimethylsulfoxide, sulfolane, catechol, ethyl lactate, acetone, butyl carbitol, monoethanolamine, butyrol lactone, diglycol amine, γ -butyrolactone, butylene carbonate, ethylene carbonate, and propylene carbonate, wherein alkyl is C₁-C₈ alkyl and aryl is C₆-C₁₀ aryl.
11. The composition of claim 8, wherein the co-solvent comprises at least one alcohol.
12. The composition of claim 8, wherein the co-solvent comprises at least one solvent species selected from the group consisting of methanol, ethanol, and isopropyl alcohol.
13. The composition of claim 8, wherein the co-solvent comprises at least one solvent species selected from the group consisting of N-methyl-, N-octyl-, and N-phenyl- pyrrolidones.
14. The composition of claim 8, wherein the co-solvent comprises at least one solvent species selected from the group consisting of ethanol and isopropyl alcohol.
15. The composition of claim 2, further comprising an inhibitor that is effective to inhibit attack of the cleaning composition on low dielectric constant layer material.

16. The composition of claim 15, wherein the inhibitor comprises at least one inhibitor species selected from the group consisting of organic acids and inorganic acids.

17. The composition of claim 15, wherein the inhibitor comprises boric acid.

18. The composition of claim 2, wherein the supercritical fluid species comprises a substantial major fraction of the cleaning composition.

19. The composition of claim 2, wherein the supercritical fluid species is present in an amount of from about 75% by weight to about 99.01% by weight, based on the total weight of the composition.

20. The composition of claim 2, wherein the supercritical fluid species is present in an amount of from about 80% by weight to about 99.01% by weight, based on the total weight of the composition.

21. The composition of claim 2, wherein the fluoro species is present in an amount of from about 0.01% by weight to about 5% by weight, based on the total weight of the composition.

22. The composition of claim 15, wherein the inhibitor is present in an amount of up to about 5% by weight, based on the total weight of the composition.

23. The composition of claim 8, wherein the co-solvent is present in an amount of up to about 25% by weight, based on the total weight of the composition.

24. The composition of claim 8, wherein the co-solvent is present in an amount of up to about 20% by weight, based on the total weight of the composition.

25. The composition of claim 8, wherein the co-solvent is present in an amount of from about 1% to about 20% by weight, based on the total weight of the composition.

26. The composition of claim 2, having the following formulation, wherein all percentages are by weight:

Carbon dioxide: 80-99.01% (w/w)

Fluoride species: 0.01-5.0% (w/w)

Low-k material attack inhibitor: 0.0-5.0% (w/w)

Co-solvent: 0-20% (w/w)

TOTAL: 100% by weight.

27. The composition of claim 2, having the following formulation, wherein all percentages are by weight:

Carbon dioxide: 80-99% (w/w)

Fluoride species: 0.01-5.0% (w/w)

Co-solvent: 1-20% (w/w)

Surfactant: 0.0-5.0% (w/w)

TOTAL: 100% by weight.

28. The composition of claim 1, comprising primary and/or secondary amine(s).

29. The composition of claim 28, further comprising co-solvent.

30. The composition of claim 28, further comprising surfactant.

31. The composition of claim 28, further comprising co-solvent and surfactant.

32. The composition of claim 28, wherein the supercritical fluid is present in an amount of from about 75% by weight to about 99.01% by weight, based on the total weight of the composition.

33. The composition of claim 28, wherein the supercritical fluid is present in an amount of from about 80% by weight to about 99% by weight, based on the total weight of the composition.

34. The composition of claim 28, comprising from about 0.01% to about 5.0% by weight of the primary and/or secondary amine(s), based on the total weight of the composition.

35. The composition of claim 29, comprising from about 1% to about 25% by weight of co-solvent, based on the total weight of the composition.

36. The composition of claim 29, comprising from about 1% to about 20% by weight of co-solvent, based on the total weight of the composition.

37. The composition of claim 30, comprising up to about 5% by weight of surfactant, based on the total weight of the composition.

38. The composition of claim 28, comprising from about 80 to about 99.01% by weight of SCCO_2 , from about 0.01% to about 5.0% by weight of primary and/or secondary amine, from about 1% to about 20% by weight of co-solvent, and optionally up to 5% by weight of surfactant, with all ingredient weight percentages being based on the total weight of the composition, and with all weight percentage amounts of such ingredients totaling to 100 weight %.

39. The composition of claim 28, wherein the supercritical fluid comprises a fluid species selected from the group consisting of carbon dioxide, oxygen, argon, krypton, xenon, ammonia, methane, methanol, dimethyl ketone, hydrogen, forming gas, and sulfur hexafluoride.

40. The composition of claim 28, wherein the supercritical fluid comprises carbon dioxide.
41. The composition of claim 28, wherein the primary and/or secondary amine(s) include at least one amine species selected from the group consisting of hydroxylamine (NH_2OH), ammonia (NH_3), alkylamines ($\text{R}-\text{NH}_2$) and dialkylamines ($\text{R}_1\text{R}_2\text{NH}$), wherein R , R_1 and R_2 are each independently selected from $\text{C}_1\text{-C}_8$ alkyl and $\text{C}_6\text{-C}_{10}$ aryl.
42. The composition of claim 29, wherein the co-solvent comprises at least one solvent species selected from the group consisting of alcohols, amides, ketones, esters, lactones, and 1,3-diones.
43. The composition of claim 29, wherein the co-solvent comprises isopropyl alcohol.
44. The composition of claim 30, wherein the surfactant comprises a non-ionic surfactant.
45. The composition of claim 1, at pressure in a range of from about 800 to about 10,000 psi.
46. The composition of claim 45, at temperature in a range of from about 20 to about 150°C.
47. The composition of claim 45, at temperature in a range of from about 40 to about 100°C.
48. The composition of claim 45, at temperature in a range of from about 75 to about 80°C.
49. A method of cleaning of a semiconductor wafer, comprising contacting the semiconductor wafer with a supercritical fluid-based cleaning composition including supercritical fluid and at least one additive selected from the group consisting of:
 - (I) fluoro species; and

(II) primary and/or secondary amine(s).

50. The method of claim 49, wherein the composition comprises fluoro species.
51. The method of claim 50, wherein the supercritical fluid comprises a supercritical fluid species selected from the group consisting of carbon dioxide, oxygen, argon, krypton, xenon, ammonia, methane, methanol, dimethyl ketone, hydrogen, forming gas, and sulfur hexafluoride.
52. The method of claim 50, wherein the supercritical fluid comprises carbon dioxide.
53. The method of claim 50, wherein the fluoro species comprises a fluorine-containing material selected from the group consisting of hydrogen fluoride (HF), ammonium fluoride (NH_4F), alkyl hydrogen fluoride (NRH_3F), dialkylammonium hydrogen fluoride ($\text{NR}_2\text{H}_2\text{F}$), trialkylammonium hydrogen fluoride (NR_3HF), trialkylammonium trihydrogen fluoride ($\text{NR}_3(3\text{HF})$), tetraalkylammonium fluoride (NR_4F), and xenon difluoride (XeF_2), wherein each R is independently selected from $\text{C}_1\text{-C}_8$ alkyl and $\text{C}_6\text{-C}_{10}$ aryl.
54. The method of claim 50, wherein the fluoro species comprises triethylamine trihydrogen fluoride.
55. The method of claim 50, wherein the fluoro species comprises ammonium fluoride.
56. The method of claim 50, wherein the composition further comprises co-solvent.
57. The method of claim 56, wherein the co-solvent comprises at least one solvent species selected from the group consisting of alcohols, amides, ketones, and esters.

58. The method of claim 56, wherein the co-solvent comprises at least one solvent species selected from the group consisting of alcohols, N-alkylpyrrolidones, N-arylprroridones, dimethylsulfoxide, sulfolane, catechol, ethyl lactate, acetone, butyl carbitol, monoethanolamine, butyrolactone, diglycol amine, γ -butyrolactone, butylene carbonate, ethylene carbonate, and propylene carbonate, wherein alkyl is C₁-C₈ alkyl and aryl is C₆-C₁₀ aryl.
59. The method of claim 56, wherein the co-solvent comprises at least one alcohol.
60. The method of claim 56, wherein the co-solvent comprises at least one solvent species selected from the group consisting of methanol, ethanol, and isopropyl alcohol.
61. The method of claim 56, wherein the co-solvent comprises at least one solvent species selected from the group consisting of N-methyl-, N-octyl-, and N-phenyl- pyrrolidones.
62. The method of claim 56, wherein the co-solvent comprises at least one solvent species selected from the group consisting of ethanol and isopropyl alcohol.
63. The method of claim 50, wherein the composition further comprises an inhibitor that is effective to inhibit attack of the cleaning composition on low dielectric constant layer material.
64. The method of claim 63, wherein the inhibitor comprises at least one inhibitor species selected from the group consisting of organic acids and inorganic acids.
65. The method of claim 63, wherein the inhibitor comprises boric acid.
66. The method of claim 50, wherein the supercritical fluid species comprises a substantial major fraction of the cleaning composition.

67. The method of claim 50, wherein the supercritical fluid species is present in the composition in an amount of from about 75% by weight to about 99.01% by weight, based on the total weight of the composition.
68. The method of claim 50, wherein the supercritical fluid species is present in an amount of from about 80% by weight to about 99.01% by weight, based on the total weight of the composition.
69. The method of claim 50, wherein the fluoro species is present in an amount of from about 0.01% by weight to about 5% by weight, based on the total weight of the composition.
70. The method of claim 63, wherein the inhibitor is present in an amount of up to about 5% by weight, based on the total weight of the composition.
71. The method of claim 56, wherein the co-solvent is present in an amount of up to about 25% by weight, based on the total weight of the composition.
72. The method of claim 56, wherein the co-solvent is present in an amount of up to about 20% by weight, based on the total weight of the composition.
73. The method of claim 56, wherein the co-solvent is present in an amount of from about 1% to about 20% by weight, based on the total weight of the composition.
74. The method of claim 50, wherein the composition has the following formulation, wherein all percentages are by weight:

Carbon dioxide: 80-99.01% (w/w)

Fluoride species: 0.01-5.0% (w/w)

Low-k material attack inhibitor: 0.0-5.0% (w/w)

Co-solvent: 0-20% (w/w)

TOTAL: 100% by weight.

75. The method of claim 50, wherein the composition has the following formulation, wherein all percentages are by weight:

Carbon dioxide: 80-99% (w/w)

Fluoride species: 0.01-5.0% (w/w)

Co-solvent: 1-20% (w/w)

Surfactant: 0.0-5.0% (w/w)

TOTAL: 100% by weight.

76. The method of claim 49, wherein the composition comprises primary and/or secondary amine(s).

77. The method of claim 76, wherein the composition further comprises co-solvent.

78. The method of claim 76, wherein the composition further comprises surfactant.

79. The method of claim 76, wherein the composition further comprises co-solvent and surfactant.

80. The method of claim 76, wherein the supercritical fluid is present in the composition in an amount of from about 75% by weight to about 99.01% by weight, based on the total weight of the composition.

81. The method of claim 76, wherein the supercritical fluid is present in the composition in an amount of from about 80% by weight to about 99% by weight, based on the total weight of the composition.
82. The method of claim 76, wherein the composition comprises from about 0.01% to about 5.0% by weight of the primary and/or secondary amine(s), based on the total weight of the composition.
83. The method of claim 77, wherein the composition comprises from about 1% to about 25% by weight of co-solvent, based on the total weight of the composition.
84. The method of claim 77, wherein the composition comprises from about 1% to about 20% by weight of co-solvent, based on the total weight of the composition.
85. The method of claim 78, wherein the composition comprises up to about 5% by weight of surfactant, based on the total weight of the composition.
86. The method of claim 77, wherein the composition comprises from about 80 to about 99.01% by weight of SCCO_2 , from about 0.01% to about 5.0% by weight of primary and/or secondary amine, from about 1% to about 20% by weight of co-solvent, and optionally up to 5% by weight of surfactant, with all ingredient weight percentages being based on the total weight of the composition, and with all weight percentage amounts of such ingredients totaling to 100 weight %.
87. The method of claim 76, wherein the supercritical fluid comprises a fluid species selected from the group consisting of carbon dioxide, oxygen, argon, krypton, xenon, ammonia, methane, methanol, dimethyl ketone, hydrogen, forming gas, and sulfur hexafluoride.

88. The method of claim 76, wherein the supercritical fluid comprises carbon dioxide.
89. The method of claim 76, wherein the primary and/or secondary amine(s) include at least one amine species selected from the group consisting of hydroxylamine (NH_2OH), ammonia (NH_3), alkylamines ($\text{R}-\text{NH}_2$) and dialkylamines ($\text{R}_1\text{R}_2\text{NH}$), wherein R , R_1 and R_2 are each independently selected from $\text{C}_1\text{-C}_8$ alkyl and $\text{C}_6\text{-C}_{10}$ aryl.
90. The method of claim 77, wherein the co-solvent comprises at least one solvent species selected from the group consisting of alcohols, amides, ketones, esters, lactones, and 1,3-diones.
91. The method of claim 77, wherein the co-solvent comprises isopropyl alcohol.
92. The method of claim 78, wherein the surfactant comprises a non-ionic surfactant.
93. The method of claim 49, wherein the contacting step is carried out at pressure in a range of from about 800 to about 10,000 psi.
94. The method of claim 93, wherein the contacting step is carried out at temperature in a range of from about 20 to about 150°C.
95. The method of claim 93, wherein the contacting step is carried out at temperature in a range of from about 40 to about 100°C.
96. The method of claim 93, wherein the contacting step is carried out at temperature in a range of from about 75 to about 80°C.